This project has as its focus the design and synthesis of polyammonium macrocyclic receptors for oxoanions of environmental importance. The basic research aspects of this project involve synthesis (and the search for improved synthetic methods), solid state structure determination and thermodynamics studies (to ascertain structural criteria for and strength of anion binding), and molecular dynamics simulations (to assess solution characteristics of the interactions between anions and their receptors). Applications-oriented goals include the fabrication of more efficient anion-selective electrodes and the use of these compounds in liquid-liquid separations. The latter goal is the subcontract with Bruce Moyer at Oak Ridge National Laboratory. This first year we have focused on nitrates and phosphates. Considerable progress has been made in the basic areas of synthesis, solid state structure, and molecular dynamics. Anion selective electrodes have also be made which show promising selectivities for oxoanions of interest. Below are described the major findings and significance in the categories of synthesis, structure and molecular dynamics, and electrode studies.

**Synthesis.** The synthesis of polyaza macrocycles which are the focus of these studies is often tedious and time-consuming. For example, the synthesis of \([24]\text{N}_4\text{O}_2\) (1) (compounds shown on page 2) usually takes approximately one month because of time-consuming purifications required during the synthesis. A major breakthrough which we have made this year is to identify other polyaza macrocycles, which also bind the desired anions, but which are simpler to synthesize via a two step Schiff base/reduction process with high yields. This is truly significant since now we can obtain large quantities of the macrocycles and do multiple studies at once (crystallizations, thermodynamics, electrode, and eventually separations). Most of our studies to date have focused on monocyclic systems (1 - 7), but we are now beginning to examine bicyclic macrocycles (8), which can be synthesized by the same method starting with the tetraamine known as tren (9).
Structural and molecular dynamics studies. We now have four crystal structures of nitrate complexes with polyaza macrocycles and one with phosphate. In all except one (1) the macrocycles are relatively flat and the nitrates hover in the surrounding area. These findings have lead us to speculate that the ether oxygens in the ring of 1 play an important structural role, allowing the macrocycle to fold more effectively, and thus to encapsulate the anion. We have also obtained a crystal structure of xx with phosphate, which is unique in that there are eight phosphates surrounding the macrocycle (which should maximally only complex six dihydrogen phosphates). This indicates to us that the macrocycle acts as a phosphate "sponge," and may well be an exceptionally suited for phosphate recognition and binding.

Our tidings from electrode studies have indicated that 3 and 4 are also promising sensors, indicating that they may have the same structural properties as 1, and so we are avidly investigating these particular macrocycles.

Plans are underway to measure association constants for all of these ligands and different oxoanions. A postdoctoral associate with considerable expertise in this area has just joined our group, and he will be primarily involved in this endeavor.

Solution molecular dynamics studies on several complexes using the program CHARMM indicate that the folded 1 unfolds in solution due to solvation effects. Hence, this has led us to begin investigations on bicyclic compounds such as 8, which are also readily synthesized by Schiff base condensations as noted above.

Because of the aromatic rings in 2 and 3, we decided to investigate whether these macrocycles can bind aromatic compounds, which are also of interest in environmental remediation efforts. We have succeeded in co-crystallizing 3 with nitrobenzene, which indicates that this may be a promising area for expansion of the project.
Electrode studies. Studies are well in progress on the utilization of the polyaza macrocycles in anion selective electrodes. To date, the three most successful compounds for selective binding of oxoanions in an electrode system appear to be 1, 3, and 4, the latter two being available in large quantities as a result of our synthetic findings. Macrocycles of similar structural types have been added to the list to be examined in attempts to enhance the selectivity. We suspect that 3 and 4 may have similar structural properties and are investigating this point.

Separations studies. (Subcontract with Bruce Moyer at Oak Ridge National Laboratory) These studies will get underway this Fall, with a Ph.D. student from our group (Arthur Reyes) spending an internship at Oak Ridge to test some of the most promising macrocycles in liquid-liquid separations. The reason that these studies have not yet begun is that we were waiting to identify superior receptors and to synthesize large quantities for use in the separations studies. The new synthetic routes and promising results from compounds 3 and 4 mean that these studies are ready to begin. Now that the studies will begin at Oak Ridge, the remaining funds in year 1 (the subcontract) will be used this Fall in addition to the funds allocated for the Oak Ridge subcontract next year.